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Distribution of hydrogen peroxide and methylhydroperoxide over the Pacific and South Atlantic Oceans

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Abstract. The gas phase hydrogen peroxide and methylhydroperoxide concentrations were measured in the troposphere over the tropical Pacific Ocean as a component of NASA's Global Tropospheric Experiment/Pacific Exploratory Mission-Tropics A field campaign. Flights on two aircraft covered the Pacific from 70°S to 60°N and 110°E to 80°W and South Atlantic from 40°S to 15°N and 45°W to 70°E, and extending from 76 to 13,000 m altitude. H_2O_2 and CH_3OOH have the highest concentrations at a given altitude at the equator and decrease with increasing latitude in both the northern and southern hemispheres. Above 4 km the gradient is substantially reduced for both H_2O_2 and CH_3OOH with latitude, and at altitudes in excess of 8 km there is no latitudinal dependence. H_2O_2 and CH_3OOH exhibit maximum mixing ratios between 1 and 2 km at all latitudes. The mean mixing ratio of H_2O_2 at the equator was 1600 ± 600 parts per trillion by volume (pptv) decreasing to 500 ± 250 pptv at latitudes greater than 55° north and south between 1 and 2 km altitude. CH_3OOH at the equator was 1400 ± 250 pptv, decreasing to 330 ± 200 pptv at high latitudes at altitudes between 1 and 2 km. The concentration of peroxides at high latitudes in the northern hemisphere was generally a factor of 2 higher than at corresponding latitudes in the southern hemisphere. The ratio of H_2O_2 to CH_3OOH was between 1 and 2 from 45°S to 35°N at altitudes below 4 km. Between 5° to 15°N the ratio is less than 1, due to preferential removal of H_2O_2 in the Intertropical Convergence Zone.

1. Introduction

The distributions of hydrogen peroxide (H_2O_2) and methylhydroperoxide (CH_3OOH) have been observed in the oceanic troposphere during NASA's Global Tropospheric Experiment (GTE) program. Over the last few years this program sponsored four field campaigns in which the peroxide mixing ratios were determined. The first was the Pacific Exploratory Mission West A (PEM-West A) where measurements were made in the western Pacific from the NASA DC-8 during September and October of 1991. The next mission was the Transport and Atmospheric Chemistry Near the Equatorial Atlantic (TRACE A) program in September to October of 1992, followed by the second phase of the Pacific Exploratory Mission (PEM-West B) in January and February of 1993. The most recent mission was PEM-Tropics A which focused on the tropical Pacific and involved both the NASA DC-8 and P3-B aircraft during September and October of 1996. The principal goals of the TRACE A mission were to assess the relative contributions of photochemistry, and large and small scale circulation features to the enhanced ozone mixing ratios observed over the tropical Atlantic Ocean. The meteorological and mission overviews were presented by *Bachmeier and Fuelberg* [1996] and *Fishman et al.* [1996], respectively. The PEM-West A and B missions and PEM-Tropics A principal goals were to enhance our understanding of the distribution of O_3 over the Pacific Ocean through an exploration of atmospheric composition and dynamics, and second, to improve our understanding of sulfur gas chemistry in the Pacific troposphere.

Hydrogen peroxide and methylhydroperoxide are important compounds in the chemical cycles of O_3 and SO_2 in the troposphere. Although oxidation of sulfur dioxide by O_3 and H_2O_2 is thermodynamically possible in the gas phase, the reactions are kinetically inhibited and do not occur to a substantial extent [*Calvert et al.*, 1985]. However, hydroperoxides and O_3 are effective aqueous oxidants of dissolved SO_2 in atmospheric aqueous phases (cloud drops, rain, and fog) [*Calvert et al.*, 1985]. Hydrogen peroxide is believed to be the dominant oxidant for SO_2 in atmospheric aqueous phases with $pH < 5$ [*Calvert et al.*, 1985]. In addition, H_2O_2 and CH_3OOH are intimately involved in the odd-hydrogen($\cdot OH$, $HO_2\cdot$, and $CH_3OO\cdot$) and odd-oxygen chemistry of the atmosphere [*Logan et al.*, 1981; *Kleinman*, 1991]. H_2O_2, CH_3OOH, and HNO_3 are the main reservoirs for these radicals in the troposphere. Their photolysis produces odd-hydrogen species, of which hydroxyl radical is the most abundant. Hydroxyl radical is the most significant oxidant and cleansing agent of the troposphere [*National Research Council (NRC)*, 1984]. Removal of H_2O_2 and CH_3OOH by reaction with hydroxyl (OH) or by deposition are the principal removal pathways for these radicals [*Logan et al.*, 1981]. Either directly or through the above radicals, hydroperoxides are involved in the conversion of sulfur, nitrogen,

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and carbon compounds to their acidic forms in atmospheric water [*Penkett et al.*, 1979; *Lind et al.*, 1987].

The gas phase kinetics of H_2O_2 and CH_3OOH formation and destruction have been studied [e.g., *Atkinson et al.*, 1993, and references therein], and their atmospheric concentration appears to be in agreement with photochemical models when the effects of rapid transport or heterogeneous processes are negligible [*Heikes et al.*, 1996b; *Jacob et al.*, 1996]. The simpler alkyl-hydroperoxides are believed to be produced by the reaction of hydroperoxyl radical with alkyl-peroxyl radicals, and lost by photolysis and reaction with OH [*Atkinson et al.*, 1993]. Consequently, in the free troposphere the concentration of H_2O_2 and CH_3OOH can be used as constraints on odd-hydrogen chemistry. Measurements of H_2O_2 which are greater than model predictions are suggestive of either higher HO_2 mixing ratios or slower removal and visa versa [*Liu et al.*, 1992].

In the lower troposphere, heterogeneous processes are comparable to gas phase mechanisms in the loss of hydroperoxides. The aqueous destruction and deposition of the hydroperoxides is dependent upon their uptake by wet aerosol, cloud, precipitation, or particulate surfaces. Generally, the uptake of soluble atmospheric species is limited by the volume of atmospheric water present, the chemical composition of the water, and the solubility of the atmospheric constituent in the resulting aqueous phase [*Jaeschke and Herrmann*, 1987]. Deposition rates to surface seawater can be estimated based upon solubility [*Liss and Merlivat*, 1986; *Sheih et al.*, 1979]. The Henry's law solubility of H_2O_2 has been determined by several groups [*O'Sullivan et al.*, 1996, and references therein]. Determinations of organic hydroperoxide aqueous solubilities are fewer in number [*O'Sullivan et al.*, 1996], but show that the Henry's law constant for CH_3OOH, for example, is 3 orders of magnitude less than for H_2O_2. The lower solubility of CH_3OOH in water makes this compound less susceptible to precipitation and surface removal [*Lind and Kok*, 1986; *Heikes et al.*, 1996a]. The difference in the production and loss rates for H_2O_2 and CH_3OOH, coupled to the difference in surface removal for these species, produce a powerful tool to examine diurnally averaged photochemistry in the troposphere. The ratio of H_2O_2 to CH_3OOH is also a good marker for recent convective activity, since H_2O_2 is preferentially removed relative to CH_3OOH.

In this paper we present the distribution of H_2O_2 and CH_3OOH in the Pacific and South Atlantic troposphere observed during several field campaigns. Sample collection and analytical procedures are briefly described, as well as the data sets used in the compilation. The geographical distributions of the peroxides are presented, and the impact of source emissions and photochemistry is explored.

2. Experiment

2.1. Field Experiments

The data sets used for this peroxide distribution were from the NASA Global Tropospheric Experiment, Pacific Exploratory Missions (GTE-PEM). The first PEM mission was PEM-West A which involved field measurements from the NASA DC-8 platform during a 6-week period from September to October 1991 [*Hoell et al.*, 1996]. The next mission was the TRACE A program, followed by the second phase of the Pacific Exploratory Mission (PEM-West B) in January and February of 1993. The most recent mission was PEM-Tropics A which involved both the NASA DC-8 and P3-B aircraft during September and October of 1996. These field programs involved measurements of a number of chemical species which contribute to understanding the chemistry of O_3 and SO_2 in the troposphere [*Hoell et al.*, this issue]. A number of these measurements were used to interpret the peroxide distributions. Since each of the instruments in the aircraft payload for the various missions had a unique duty cycle, their respective measurements were merged to the peroxide time base for each mission. Observations from instruments with a shorter time resolution than the peroxides were averaged over the peroxide duty cycle. If a species was not directly measured during the peroxide sample interval, it was treated as missing. If a species sample interval exceeded the peroxide sample interval, the species concentration was assumed to remain constant in our data merge for multiple peroxide sample intervals. For PEM-West A there was a 2.5 min sample resolution for the peroxides, and a 3 min merged data product was used. For the other missions a 5 min sample resolution was used for the peroxide analyses resulting in a 5 min merged data product. The peroxide measurements from all the missions in a 2.5° × 2.5° latitude-longitude grid were averaged using a near-neighbor algorithm. The near-neighbor algorithm reads x, y, and z data (latitude, longitude, peroxide concentration for a given altitude bin) and assigns an average value to each grid node that has one or more points within a given radius centered on the node. The average value is computed as the weighted mean of all points inside the search radius. The weighting function was $w(r) = 1.0/(1 + d^2)$; where $d = (3 \times r)/(\text{search radius})$ and r is the distance of the point from the node [*Wessel and Smith*, 1995]. The result was plotted for that grid using the Generic Mapping Tools software [*Wessel and Smith*, 1995].

2.2. Analytical Methods

Gas phase H_2O_2 and CH_3OOH were collected with continuous flow glass cyclone separators [*Lazrus et al.*, 1986] and quantified using the high performance liquid chromatographic (HPLC) fluorometric method described by *Lee et al.* [1995] [*Kok et al.*, 1995]. Hydroperoxides were separated by reverse phase HPLC on a 5μ Inertsil ODS-2 PEEK column (4.6 mm × 250 mm, Metachem) followed by a postcolumn derivatization reaction forming a fluorescent dimmer. The peroxidase catalyzed dimerization of *p*-hydroxyphenyl acetic acid occurs in the presence of peroxy functional groups at elevated *p*H. Formation of the fluorescent dimmer is proportional to the concentration of a given hydroperoxide [*Kok et al.*, 1995; *Lee et al.*, 1995]. Details regarding the system configurations for the PEM-West A and B and TRACE A programs are given by *Heikes et al.* [1996a, b] and *Lee et al.* [1998], respectively.

2.3. Aircraft Instrument Configuration PEM Tropics A

The apparatus used during PEM-Tropics A on the DC-8 and P3-B were identical. The systems from both aircraft were run side by side in the laboratory and gave comparable measurements within stated precision and detection limits. In the field, common aqueous stock solutions of H_2O_2 and CH_3OOH were used. Before and after the field program, mass flow controllers and pump-tube calibrations were performed using the same devices. Therefore systematic biases in calibration were not expected.

Side-by-side flight comparisons were not made between the two aircraft measurement systems owing to the vastly different operating characteristics of the two aircraft (turbo-prop; fan jet) and issues of safety away from direct radar control in the

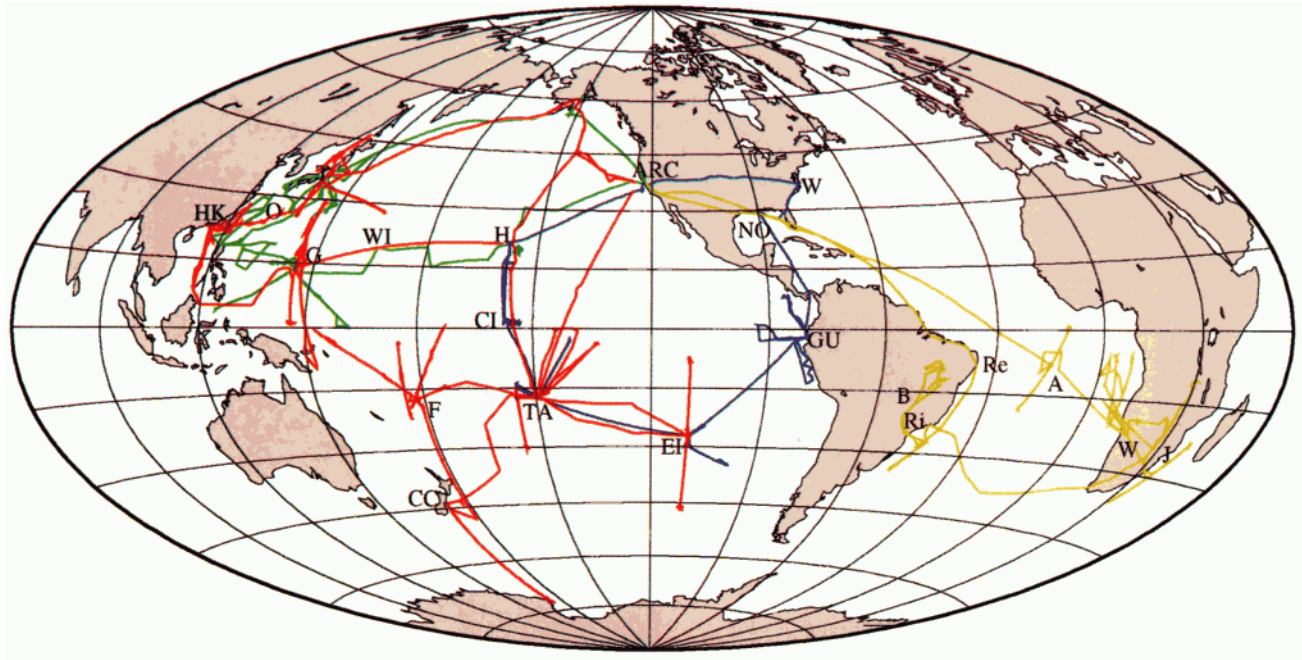

Plate 1. Flight tracks for the different GTE missions. PEM-West A is in green, PEM-West B is in red, PEM-Tropics A DC-8 flights are in pink, and the P3-B flights are in blue. TRACE A flights are shown in yellow. A (northern hemisphere), Anchorage; A (southern hemisphere), Ascension Island; ARC, Ames Research Center; CC, Christchurch; CI, Christmas Island; EI, Easter Island; F, Fiji; G, Guam, GU, Guayaquil; H, Honolulu; HK, Hong Kong, J, Johannesburg; NO, New Orleans, O, Okinawa; T, Tokyo, TA, Tahiti; Re, Recife, Ri, Rio de Janeiro; W (northern hemisphere), Wallops Island; W (southern hemisphere), Warmbad; and WI, Wake Island.

flight study region. However, flight plans did call for the two aircraft to sample in the same geographic region in air masses thought to have similar (identical) air mass histories and chemistries. Measurement comparisons from the same geographic region showed identical distributions, medians, and variations. For flights where direct comparison between aircraft was thought to be possible, variance in other measured parameters suggests that the aircraft may not have occupied the same air masses.

Two HPLC systems were flown on the DC-8 which resulted in a sample interval of 2.5 min. With one system on the P3-B, the sample interval was 5 min. The sample frequency is limited by the elution time difference between H_2O_2 and CH_3OOH. H_2O_2 and CH_3OOH were the principal hydroperoxides detected with the HPLC system during the PEM-Tropics field campaign. Other hydroperoxides would have had to exceed 100 pptv to be observed quantitatively with our analytical system, based upon the detection limits given by *Lee et al.* [1995]. The analytical system was composed of a collection system for the gas phase hydroperoxides, and the HPLC technique described above for quantifying the individual hydroperoxides.

Air samples were brought into the aircraft through 0.95 cm OD (0.64 cm. ID) PFA Teflon inlets which were identical for both aircraft. The inlets were mounted at nearly a 135° angle to the oncoming airstream and protruded 2.54 cm into the airstream 3.8 cm behind a ramp. The conical shape and the position of the ramp relative to the Teflon inlet were designed to exclude atmospheric hydrometeors and optimize gas phase sampling. The entire conical inlets were 40.6 cm off the airframe of the aircrafts, well out of the aircrafts respective boundary layers at the inlet locations. An excess of ultrahigh purity (UHP) zero air flowed through the inlet during operation on the ground and at takeoff and landing to minimize contamination of the inlet. The air sample flow rate for the HPLC systems was 2 standard liters per minute (sLpm) (STP = 1 atm and 273 K). The aqueous collection solution flow rates were nominally 0.4 mL/min. Collection solution flow rates were calibrated gravimetrically. The air sample flow rates were regulated using low-pressure drop mass flow controllers (MKS Instruments Corp.) and remained constant up to pressure altitude of 13 km. The flow rates were calibrated with a digital flow meter (Gilibrator, Gilson Instruments). During all of the flights, gas flow rate, pressure, and coil temperatures were continuously monitored and recorded on a personal computer. The temperatures in the cyclone separators were monitored with thermisters (Deban Enterprises, Inc.), and the pressure was determined with an absolute pressure transducer (MKS Instruments Corp.).

Collection solution and water blanks were taken either by passing UHP zero air through the inlet and collection coil, or by passing the air sample stream through a Hopcolite trap (Mine Safety Appliance) and into the collection coil. Both these approaches result in a peroxide free air stream passing through the collection coil, and any analytical signal is a result of peroxides in the reagents. Reagent blanks for H_2O_2 can be appreciable and variable depending on water quality and the ambient levels of H_2O_2 where the reagents were prepared. A detectable reagent blank for CH_3OOH has not been observed to date. Calibrations were performed using at least four different aqueous mixing ratios of H_2O_2 and CH_3OOH. Standards were prepared prior to analysis by serial dilution of primary stock H_2O_2 and CH_3OOH standards. The H_2O_2 stocks were prepared by the procedures given by *Lee et al.* [1995], and CH_3OOH stocks were synthesized [*Rieche and*

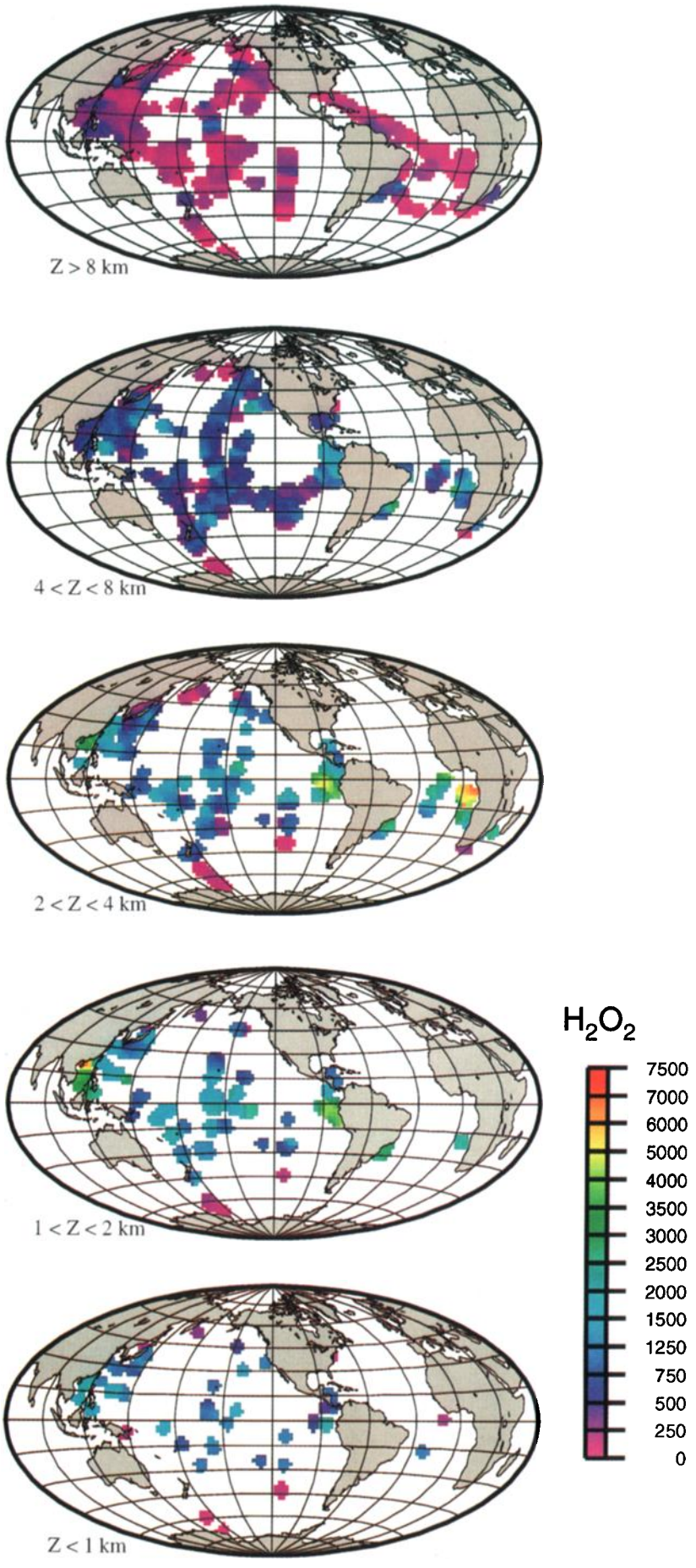

Plate 2. The distribution of hydrogen peroxide in the troposphere over the Pacific and South Atlantic Oceans as a function of altitude; the mixing ratios are in pptv.

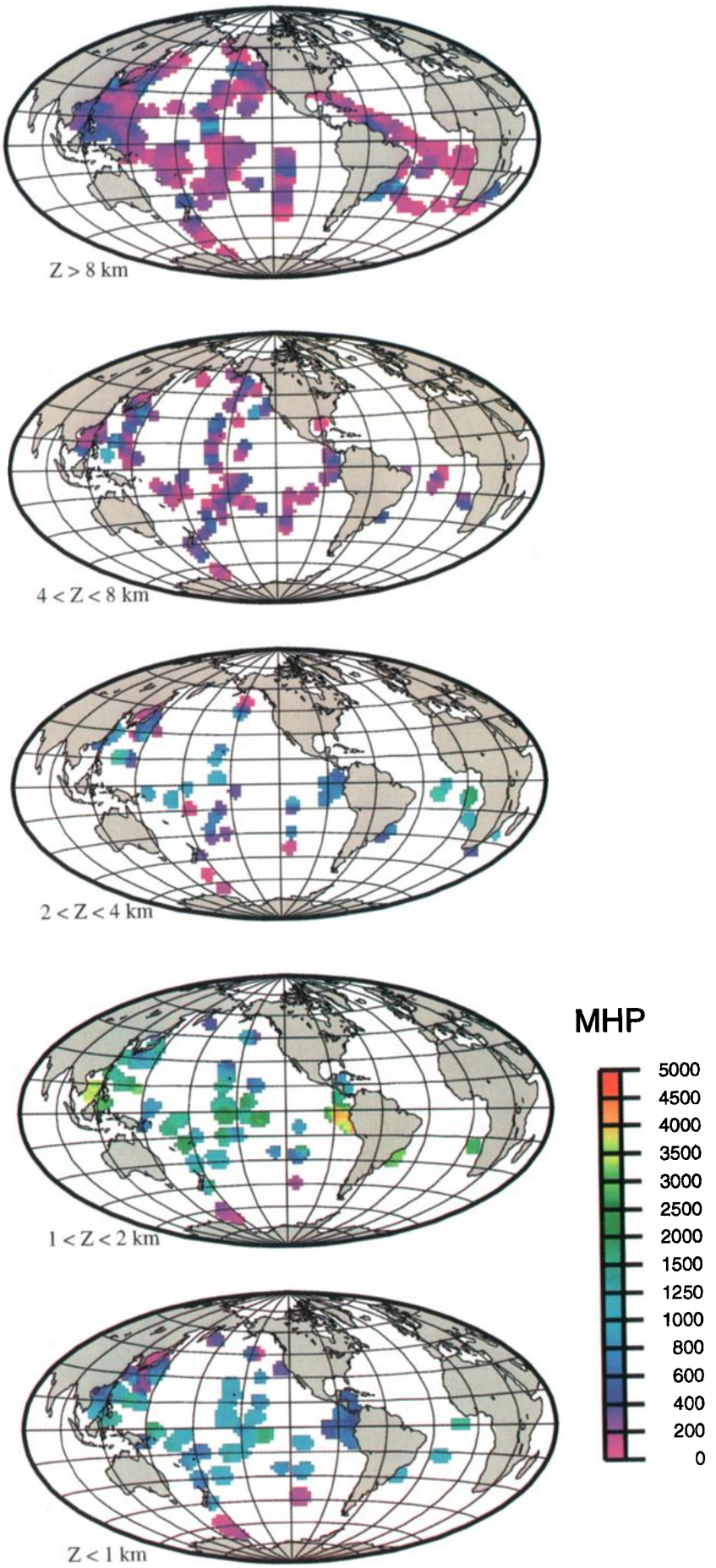

Plate 3. The distribution of methylhydroperoxide in the troposphere over the Pacific and South Atlantic Oceans as a function of altitude; the mixing ratios are in pptv.

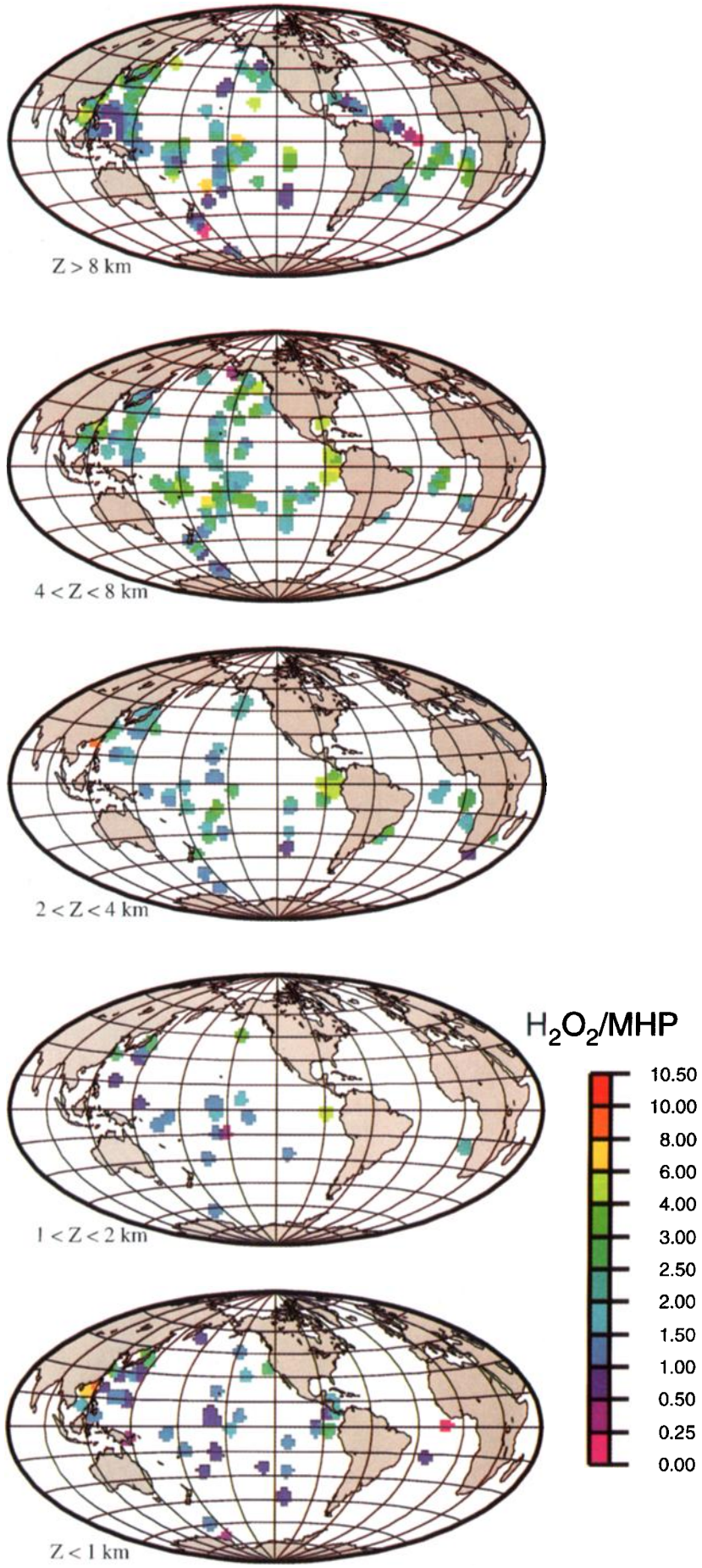

Plate 4. The distribution of the ratio of hydrogen peroxide to methylhydroperoxide in the troposphere over the Pacific and South Atlantic Oceans as a function of altitude; the mixing ratios are in pptv.

Table 1. Selected Species Concentrations and Ratios for the GTE Field Missions

Species	Mean	s.d.	Number	Range
		PEM-West A Data		
H_2O_2[a]	844	674	1,699	38–5,667
CH_3OOH[a]	603	495	1,600	51–2,398
O_3[b]	36.3	23.3	1,699	6.5–268
C_2Cl_4[a]	4.18	3.19	965	0.1–35.2
C_3H_8/C_2H_6[c]	0.11	0.07	160	0.02–0.39
C_2H_2/CO[c]	0.75	0.79	127	0.032–4.86
		PEM-West B Data		
H_2O_2	627	912	1,626	15–11,500
CH_3OOH	278	311	1,519	15–2,692
O_3	50.7	44.3	1,626	8.7–507.6
C_2Cl_4	9.7	6.7	1,319	0.74–54.5
C_3H_8/C_2H_6	0.18	0.12	1,362	0.04–0.59
C_2H_2/CO	1.98	1.41	1,295	0.09–8.63
		PEM-T Data		
H_2O_2	797	749	3,472	16–6,500
CH_3OOH	482	379	3,144	26–2,532
O_3	42.8	24.7	3,472	5.88–302.91
C_2Cl_4	1.59	0.87	2,773	0.10–16.13
C_3H_8/C_2H_6	0.071	0.036	2,845	0.018–0.49
C_2H_2/CO	0.81	0.41	2,773	0.19–3.54
		TRACE A Data		
H_2O_2	1,090	1,776	1,250	11–14,300
CH_3OOH	494	507	1,053	20–2,420
O_3	65.7	30.6	1,250	21.4–302.5
C_2Cl_4	3.79	4.51	819	0.20–77
C_3H_8/C_2H_6	0.10	0.060	879	0.018–0.77
C_2H_2/CO	1.29	0.84	871	0.09–12.96

[a]Concentration in pptv.
[b]Concentration in ppb.
[c]Ratio of concentration in pptv/ppbv.

Hitz, 1929] and calibrated using procedures of *Lee* [1995]. The collection efficiency of the coils for H_2O_2 and CH_3OOH was empirically determined by substituting aqueous standards and blanks for the collection solution in the coils. The H_2O_2 collection efficiency was always greater than 98%, while the CH_3OOH collection efficiency ranged from 50 to 70%. Uncertainty in the collection efficiency accounted for the largest portion of the estimated uncertainty in the reported mixing ratios of CH_3OOH. Detection limits for H_2O_2 and CH_3OOH were 30 and 50 pptv, respectively (3 times the standard deviation of the blank). The estimated accuracy for each measurement is available in the GTE database and was calculated through a propagation of errors, rounded to the nearest 10 pptv. These values include the uncertainties in aqueous peroxide standards, blanks, gas flow rates, aqueous flow rates, and collection efficiency for CH_3OOH.

3. Results

The PEM-Tropics A field program added another 3472 observations of peroxide mixing ratios in the Pacific troposphere which nearly doubled the available data set. The geographic location of the peroxide measurements are shown in Plate 1. The mean, standard deviations, and ranges for selected chemical species are presented in Table 1 for the four field programs. A statistical comparison of the average mixing ratios for each species between field campaigns was performed to identify significant differences at the 99.5% confidence level. Although the standard deviation about the means overlap for the different field campaigns, the t test is dominated by the large sample size, $n > 1000$ for most species, and significant differences are observed. Only the H_2O_2 and C_2H_2/CO during PEM-West A and PEM-Tropics A have average mixing ratios that are not significantly different. The differences for the remaining species are significant between PEM-West A and PEM-Tropics A. The greatest differences in the average mixing ratio for the chemical species are between PEM-West A and B, and PEM-West B and PEM-Tropics A. Since the PEM-West A and PEM-Tropics A field programs occurred at the same time of year September to October, and PEM-West B occurred from January to March, the differences in the mean mixing ratios of these species may reflect seasonally driven changes in the species.

The spatial distribution of H_2O_2, CH_3OOH, and the ratio of H_2O_2 to CH_3OOH is shown in Plates 2–4. Observations from the different missions in a given 2.5° × 2.5° latitude-longitude grid were averaged in five altitude bins, 0-1, 1-2, 2-4, 4-8, and >8 km. The lowest H_2O_2 and CH_3OOH mixing ratios are found at altitudes >8 km where levels are generally <360 and <250 pptv for H_2O_2 and CH_3OOH, respectively Plates 2c and 3c. These species exhibit maxima between 1 and 2 km altitude. The spatial distribution of the ratio of H_2O_2 to CH_3OOH is shown in Plates 4a–4c. Ratios >2 occur in areas impacted by pollution plumes which is consistent with observations from PEM-West B [*Heikes et al.*, 1996a]. Very high ratios, >6, are observed in recent continental outflow near Asia and off the coast of South America. These high ratios occur in the 2–4 or 4–8 km altitude range Plates 4b and 4c. The high ratios observed in the South Pacific near 20°S and 180°W were associ-

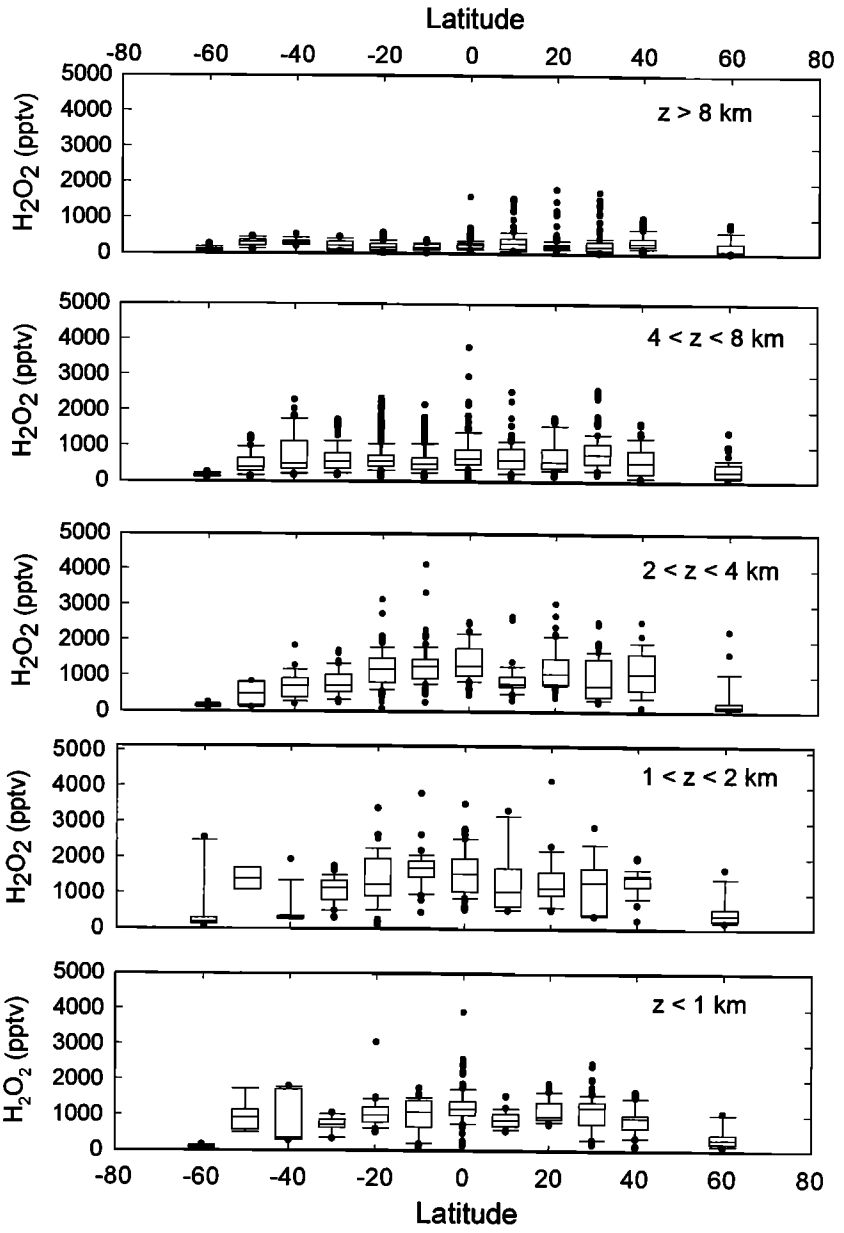

Figure 1. The latitudinal distribution of hydrogen peroxide as a function of altitude for longitudes >155°E and <245°E. In the box and whisker plots the center line is the median, the box represents the 25th and 75th percentile, and the whiskers are the 10th and 90th percentile. The solid symbols are the data points outside the 10th and 90th percentile.

ated with biomass burning plumes which are believed to have originated over Africa [*Fuelberg et al.*, this issue]. In the central Pacific away from pollutant sources, ratios <1 are observed in the 2–4 km and 0–1 km altitude bins associated with convective activity in the ITCZ and SPCZ [*Gregory et al.*, this issue].

The latitudinal distributions of H_2O_2, CH_3OOH, and the ratio are presented in Figures 1–3 in different altitude bins. Measurements at longitudes <155°E and >245°E have been removed. This removes the influence of large local pollution sources from South America and southern Asia. The data were combined in 10° latitude intervals for the box and whisker plots, for example, the 20°N box represents data between 15° and 25°N. H_2O_2 and CH_3OOH have the highest mixing ratios in a given altitude bin at the equator and decrease with increasing latitude in both the northern and southern hemispheres. Above 4 km the gradient is substantially reduced for both H_2O_2 and CH_3OOH with latitude. H_2O_2 and CH_3OOH exhibit maximum mixing ratios between 1 and 2 km at all latitudes. The mean mixing ratio of H_2O_2 at the equator is 1600 ± 600 pptv decreasing to 500 ± 250 pptv at latitudes >55° north and south at 1–2 km. CH_3OOH at the equator is 1400 ± 250 pptv, decreasing to 330 ± 200 pptv at high latitudes between 1 and 2 km. In general, the decrease in peroxide mixing ratios with latitude is asymmetric about the equator with the mixing ratios at high latitudes in the southern hemisphere about a factor of 2 below levels in the northern hemisphere at similar latitudes. The median ratio of H_2O_2 to CH_3OOH is between 1 and 2 from 45°S to 35°N at altitudes from 0 to 4 km,

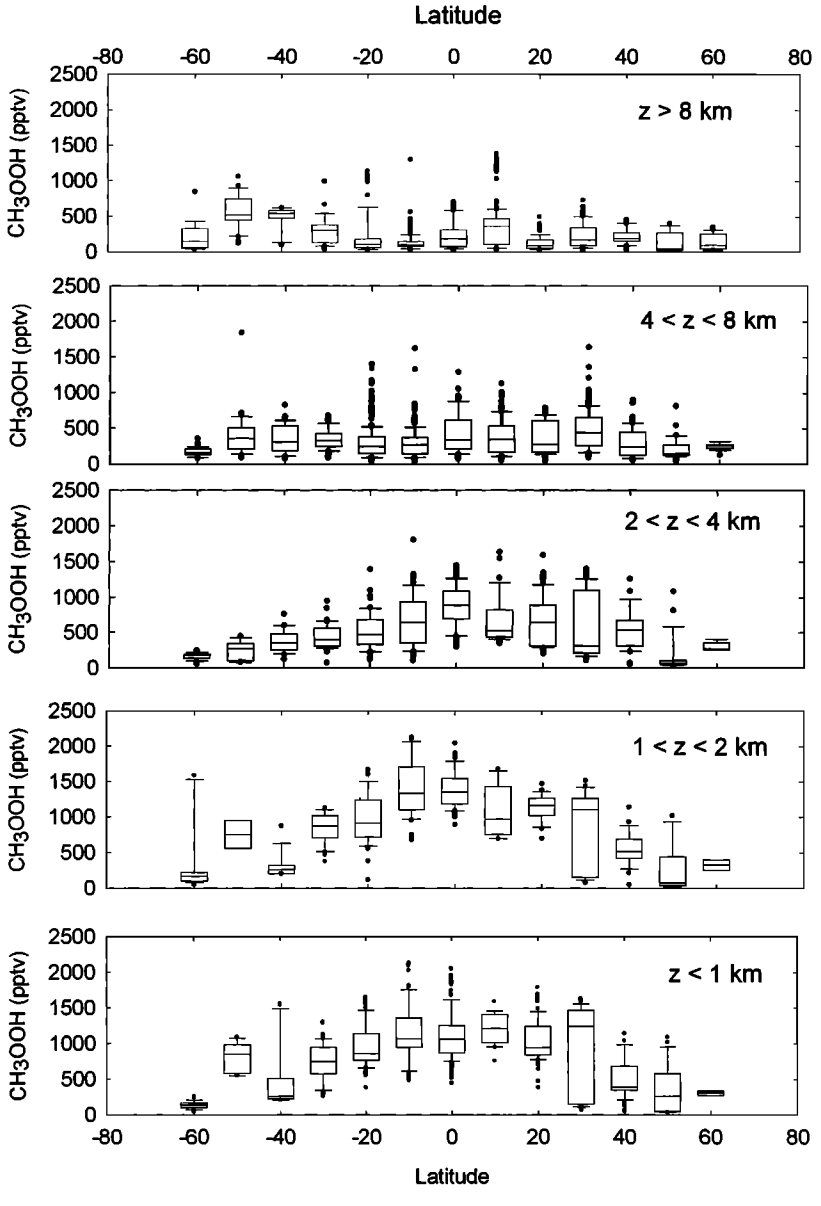

Figure 2. The latitudinal distribution of methylhydroperoxide as a function of altitude for longitudes >155°E and <245°E. See Figure 1 for an explanation of the box and whisker plots.

with the exception of 10°N (Figure 3). Below 4 km from 5°N to 15°N the ratio is <1 associated with H_2O_2 removal in the ITCZ. Above 4 km the ratio exhibits greater variability possible due to the influence of pollution plumes. At altitudes >8 km the observed mixing ratios approach the analytical detection limit which introduces variability in the ratio.

4. Discussion

The greatest similarities in the mean levels of the chemical species in Table 1 exist between the PEM-West A and PEM-Tropics A field programs. These programs occurred during the same time period, September to October, in different years and covered similar regions and altitudes. However, most of the flight hours in PEM-Tropics A were in the central, tropical Pacific, and in PEM-West A, most were in the western Pacific. PEM-West B also sampled in the western Pacific region, but during January and March. It is difficult to attribute the differences in the mean mixing ratios between PEM-West B and the other field programs to seasonally driven changes in photochemistry or transport regimes which would potentially alter the observed distributions. Some of the differences in the mean mixing ratios between the field programs are likely seasonally driven, but another component is the difference in sampling locations and altitudes during the programs. Future case studies will examine differences observed between flights in the different field programs from similar locations and altitudes to overcome this problem.

Although the mean mixing ratio for the different programs is not the best method to examine seasonal changes, some insight regarding regional conditions is possible. For example, the mixing ratio of C_2Cl_4, which is an anthropogenic gas and a tracer of urban emissions, can be used to assess the impact of local pollution sources to the region. During PEM-Tropics A the average C_2Cl_4 concentration, 1.59 ± 0.87 pptv, was more

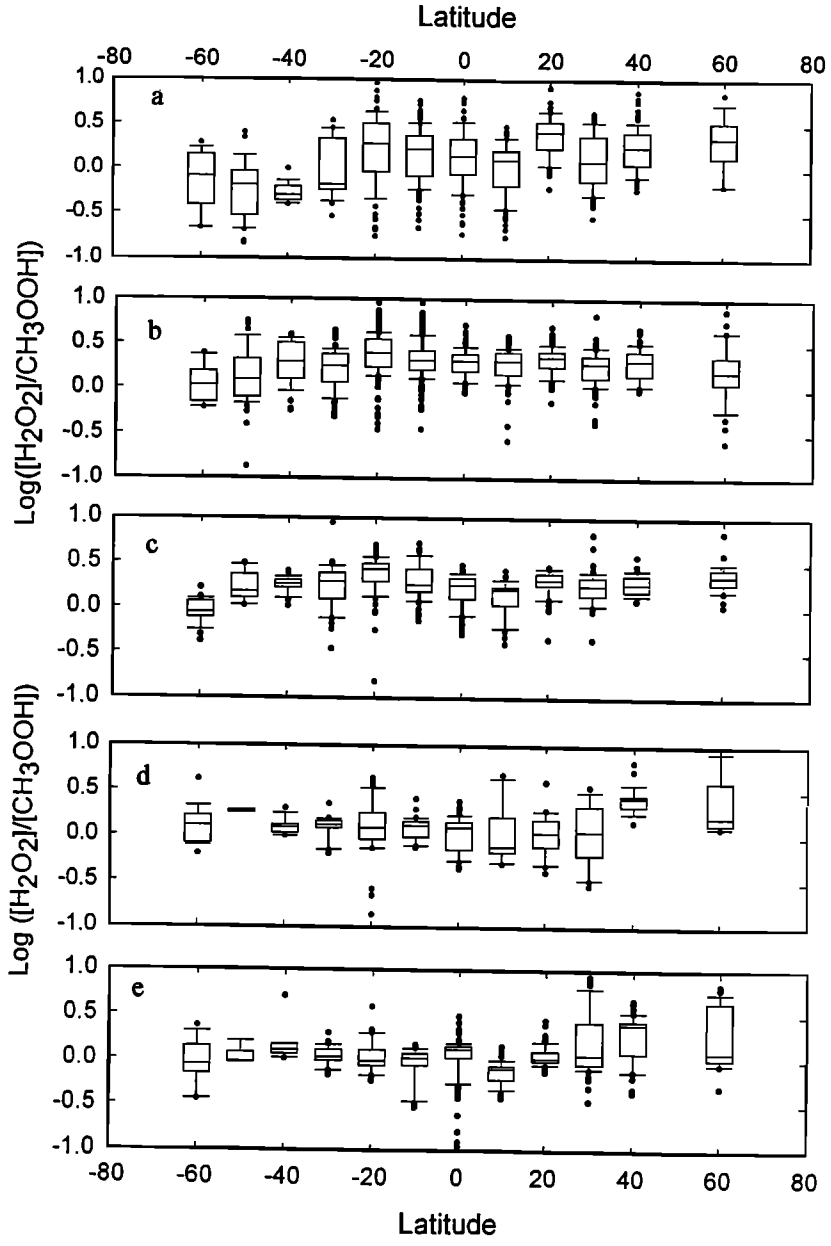

Figure 3. The latitudinal distribution of the ratio of hydrogen peroxide to methylhydroperoxide as a function of altitude for longitudes >155°E and <245°E; (a) $z > 8$ km, (b) $4 < z < 8$ km, (c) $2 < z < 4$ km, (d) $1 < z < 2$ km, and (e) $z < 1$ km. See Figure 1 for an explanation of the box and whisker plots.

than a factor of 2 lower than during PEM-West A and B, 4.18 ± 3.19 and 9.7 ± 6.7 pptv, respectively. Most of the flight hours during PEM-West A and B were in the western Pacific near Asia, while PEM-Tropics A focused on the central equatorial Pacific. The substantially lower levels observed during PEM-Tropics A indicate that the central tropical Pacific region is less impacted by local pollution sources than the western Pacific [*Blake et al.*, 1996]. *Smyth et al.* [1996] developed the acetylene to carbon monoxide ratio C_2H_2/CO (lifetime of 1 week to months) as a measure of air mass processing, which is similar to the use of the propane to ethane ratio, C_3H_8/C_2H_6 (days/weeks) [*Gregory et al.*, 1996]. Processing of the air mass occurs through photochemical oxidation by hydroxyl or by mixing continentally influenced air masses with photochemically processed air. In essence, these ratios are proxies for the age of the air mass. The higher the ratios the more recent an air mass was exposed to surface emissions. Observed H_2O_2 was independent of the processing ratios. The C_2H_2/CO ratio in PEM-Tropics A is 2.4 times less than in PEM-West B and similar to PEM-West A, supporting the notion that on average the air sampled during PEM-Tropics A had been away from the source region longer. A similar trend is observed in the C_3H_8/C_2H_6 ratios for the two field programs (Table 1). Both the concentration of C_2Cl_4 and the "processing ratios" of the air sampled during PEM-Tropics A indicate that air in the tropical Pacific is generally more processed and less influenced by local pollution sources than in the western Pacific. Consequently, the latitudinal peroxide distributions in the central Pacific are mainly a result of in situ photochemical process, rather than transport from continental regions. *Slemr and Tremmel* [1994]

observed a similar latitudinal distribution of peroxides in the lower troposphere in the Atlantic Ocean from 54°N to 51°S with shipboard measurements. They were able to model the H_2O_2 distribution using an analytical steady state expression for H_2O_2 using measurements of H_2O and O_3 and a wind-driven H_2O_2 deposition rate.

Although much of the peroxide distribution appears to be controlled by local photochemistry in the central Pacific, long-range transport of pollution plumes does influence the atmospheric chemistry of the tropical and southern Pacific. During PEM-Tropics A at altitudes from 2 to 8 km, plumes and discrete layers were sampled repeatedly on flights from Tahiti and Easter Island with elevated O_3, CO, and hydrocarbon ratios [*Fuelberg et al.*, this issue; *Talbot et al.*, this issue; *J. A. Logan et al.*, unpublished manuscript, 1998]. The hydrocarbon ratios suggest the ages of the plumes ranged from several days to over a week. Logan et al. examines the impact of these plumes on the regional photochemistry of the South Pacific.

In contrast to the latitudinal distribution of the peroxides, the longitudinal distributions are dominated by proximity to anthropogenic sources. The highest levels of the peroxides encountered in the Pacific troposphere were observed in the Celebes Sea south of the Philippines, 125°E during PEM-West A, near Taiwan during PEM-West B, and off the coast of Equador during PEM-Tropics A. In all of these regions high levels of H_2O_2 and CH_3OOH were observed in pollution plumes, levels in excess of 5000 and 2500 pptv, respectively. Some influence of the northern hemispheric pollution sources is also evident in the latitudinal distributions. At high latitudes in the northern hemisphere the peroxides are generally a factor of 2 higher than corresponding latitudes in the southern hemisphere.

The presence of the ITCZ is also evident in the peroxide distributions. A ratio of H_2O_2 to CH_3OOH less than 1 is indicative of heterogeneous removal of H_2O_2 relative to CH_3OOH (Figure 3), based upon the analysis of convective data over Brazil [*Pickering et al.*, 1996], near the Asian coast [*Heikes et al.*, 1996a], near the ITCZ in PEM-Tropics A [*Cohan et al.*, this issue], and the model studies of *Jaegle et al.* [1997] and *Prather and Jacob* [1997] (unpublished model results). The median mixing ratio of H_2O_2 is lower in the 10°N latitude bin than at the adjacent latitudes (Figure 1). During the PEM-Tropics A flights that encountered the ITCZ, its location ranged from 7° to 11°N at the locations of the aircraft crossings (138° to 155°W) [*Gregory et al.*, this issue]. The general features in the distribution of the peroxides with latitude, longitude and altitude have been observed in four field programs spanning several years. Since these features are consistent from year to year, replication of these features could provide a useful bench mark for the evaluation of atmospheric model performance.

5. Conclusions

Mixing ratios of H_2O_2 and CH_3OOH were determined in the troposphere over the Pacific Ocean as a component of NASA's Global Tropospheric Experiment/Pacific Exploratory Mission-Tropics A. The latitudinal distribution of peroxides in the central Pacific appears to be driven by in situ photochemistry. H_2O_2 and CH_3OOH exhibited the highest mixing ratios in a given altitude bin at the equator and decrease with increasing latitude in both the northern and southern hemispheres. Above 4 km the gradient was substantially reduced for both H_2O_2 and CH_3OOH with latitude. At all latitudes, both species had the highest mixing ratios between 1 and 2 km. The mean mixing ratio of H_2O_2 at the equator is 1600 ± 600 pptv decreasing to 500 ± 250 pptv at latitudes greater than 55° north and south. CH_3OOH at the equator is 1400 ± 250 pptv, decreasing to 330 ± 200 pptv at high latitudes. The ratio of H_2O_2 to CH_3OOH was between 1 and 2 from 45°S to 35°N at altitudes below 4 km. Between 5° and 15°N the ratio is <1, due to preferential removal of H_2O_2 in the ITCZ. The distribution of the peroxides about the equator is asymmetric with the mixing ratios at high latitudes in the southern hemisphere about a factor of 2 below levels in the northern hemisphere at similar latitudes. This may be a result of local pollution sources in the northern hemisphere influencing regional peroxide levels at high latitudes. The longitudinal distribution of the peroxides is dominated by proximity to local source regions in Asia and South America. The highest levels of the peroxides encountered in the Pacific troposphere were observed in pollution plumes south of the Philippines, near Taiwan, and off the coast of Equador.

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